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(54) **Fungicides for the control of take-all disease of plants**

Fungizide für die Kontrolle der Wurzelerkrankung von Pflanzen

Fongicides pour contrôle des maladies des racines des plantes

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- **THE JOURNAL OF ORGANIC CHEMISTRY** vol.
54, 1989, pp. 4372-4385, R.J. MILLS et al.
- **CHEMICAL ABSTRACTS**, vol. 99, 1983,
Columbus, Ohio, US, abstract no. 176047d

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Description

Field of the Invention

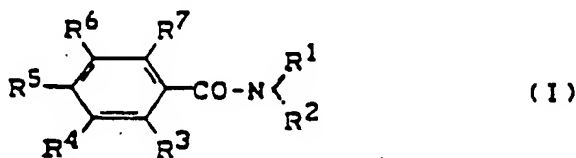
[0001] This invention relates to a method for the control of Take-All disease in plants, particularly cereals, by the use of certain substituted aryl compounds, some of which are novel, and fungicidal compositions for carrying out the method.

Background of the Invention

[0002] Take-all disease is a serious problem in the production of cereals, particularly wheat and barley. It is caused by the soil-borne fungus *Gaeumannomyces graminis* (Gg). The fungus infects the roots of the plant, and grows throughout the root tissue, causing a black rot. The growth of the fungus in the roots and lower stem prevents the plant from obtaining sufficient water and/or nutrients from the soil, and is manifested as poor plant vigor and, in severe instances of disease, by the formation of "whiteheads," which are barren or contain few, shriveled grains. Yield losses result.

[0003] Currently the primary means of avoiding crop loss due to infestation of the soil by Gg has been to rotate the crop grown to one which is resistant to Gg. However, in areas where the primary crops are cereals, rotation is not a desirable practice, and an effective control agent is greatly desired.

[0004] EPO-0243668 discloses N-substituted, benzamides of formula (I)



wherein

R¹ is H or alkyl.

R² is halogenoalkyl having more than one C-atom or halogen substituted or halogenoalkyl-substitute cycloalkyl, R³, R⁴, R⁵, R⁶ and R⁷ are the same or different and mean hydrogen, halogen, nitro, alkyl, halogenoalkyl, halogenoalkoxy, halogenoalkylthio or -CONR¹R².

[0005] In formula (I) the substituents R³ or R⁷ may be alkyl, halogenoalkyl, halogenalkoxy or halogenalkylthio (see page 1 18-22). Such compounds are useful as insecticides and nematocides and are formulated with agriculturally acceptable carriers (see page 13).

[0006] J.Org.Chem., Vol.54, 1989, pp4372-4385 discloses certain substituted N,N-diethylbenzamides when discussing a new general methodology in aromatic chemistry based on silicon protection of preferred ortho metalation sites in benzamides and O-methyl groups in O-toluides.

[0007] WO 91/01311 discloses substituted 5-carboxanilidothiazoles useful as fungicides (see pages 3-6).

[0008] J.Chem.Soc., 1963, pp1776-1781 discloses the compound 2-(2-naphthyl)-3-(methoxycarbonylamino)-benzothiofene and

[0009] J.Org.Chem, 1985, Vol.50(22), pp 4362-4368 discloses on page 4366, N-tert-butyl-3-(trimethylsilyl)thiophene-2-carboxamide = the disclaimer 2-(tert-butylaminocarbonyl)-3-(trimethylsilyl)thiophene.

[0010] Tetrahedron Letters, 1985, Vol.26(9), pp 1149-52 - discloses the compounds :

2-(diethylaminocarbonyl)-3,5-bis(trimethylsilyl)thiophene)

2-(diethylaminocarbonyl)-3-(trimethylsilyl)thiophene,

2-(diethylaminocarbonyl)-3-(trimethylsilyl)-5-(methylthio)thiophene (see page 1151).

and

2-(diethylaminocarbonyl)-3-(methylthio)-5-(trimethylsilyl)thiophene (second last compound in the Table).

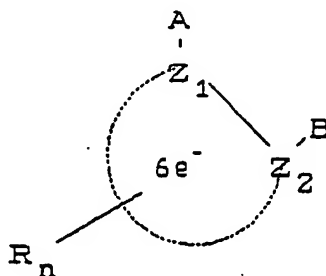
[0011] Synthesis, 1990, Vol. 10, pp915-917 - discloses 2-(tert-butylaminocarbonyl)-3-(trimethylsilylmethyl)thiophene (compound 5) and 2[N-methyl-N-(tert-butyl)aminocarbonyl]-3-(trimethylsilylmethyl)thiophene (compound 6).

[0012] It is an object of this invention to provide an effective method for control of Take-all disease in plants. It is a further object of this invention to provide compounds that control the growth of Gg in the soil so as to reduce crop loss.

It is still a further object of this invention to provide fungicidal compositions that may be used for control of Take-all disease.

Summary of the Invention

[0013] The present invention provides a method of controlling disease caused by *Gaeumannomyces* species in plants comprising applying to the plant locus, that is, the plant itself, its seed, or the soil, a fungicidally effective amount of a fungicide of the formula



wherein Z_1 and Z_2 are C and are part of an aromatic ring which is thiophene;

A is selected from $-C(X)$ -amine, $-C(O)-SR_3$, $-NH-C(X)R_4$, and $-C(=NR_3)-XR_7$;

B is $-W_m-Q(R_2)_3$ or selected from o-tolyl, 1-naphthyl, 2-naphthyl, and 9-phenanthryl, each optionally substituted with halogen or R_4 ;

Q is C, Si, Ge, or Sn;

W is $-C(R_3)_pH_{(2-p)}^-$ when Q is Si, Ge or Sn; or when Q is C, W is selected from $-N(R_3)_mH_{(1-m)}^-$, $-S(O)_p^-$, and $-O^-$;

X is O or S;

n is 0, 1, or 2;

m is 0 or 1;

p is 0, 1, or 2;

each R is independently selected from

a) halo, formyl, cyano, amino, nitro, thiocyanato, isothiocyanato, trimethylsilyl, and hydroxy;

b) C1-C4 alkyl, alkenyl, alkynyl, C3-C6 cycloalkyl, and cycloalkenyl, each optionally substituted with halo, hydroxy, thio, amino, nitro, cyano, formyl, phenyl, C1-C4 alkoxy, alkylcarbonyl, alkylthio, alkylamino, dialkylamino, alkoxycarbonyl, (alkylthio) carbonyl, alkylaminocarbonyl, dialkylaminocarbonyl, alkylsulfinyl, or alkylsulfonyl;

c) phenyl, furyl, thienyl, pyrrolyl, each optionally substituted with halo, formyl, cyano, amino, nitro, C1-C4 alkyl, alkenyl, alkynyl, alkoxy, alkylthio, alkylamino, dialkylamino, haloalkyl, and haloalkenyl;

d) C1-C4 alkoxy, alkenoxy, alkynoxy, C3-C6 cycloalkyloxy, cycloalkenyloxy, alkylthio, alkylsulfinyl, alkylsulfonyl, alkylamino, dialkylamino, alkylcarbonylamino, aminocarbonyl, alkylaminocarbonyl, dialkylaminocarbonyl, alkylcarbonyl, alkylcarbonyloxy, alkoxycarbonyl, (alkylthio)carbonyl, phenylcarbonylamino, phenylamino, each optionally substituted with halo;

wherein two R groups may be combined to form a fused ring;

each R_2 is independently selected from alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl and phenyl, each optionally substituted with R_4 or halogen; and wherein, when Q is C, R_2 may also be selected from alkoxy, alkylthio, alkylamino, and dialkylamino;

wherein two R_2 groups may be combined to form a cyclo group with Q;

R_3 is C1-C4 alkyl;

R_4 is C1-C4 alkyl, haloalkyl, alkoxy, alkylthio, alkylamino, or dialkylamino;

R_7 is C1-C4 alkyl, haloalkyl, or phenyl, optionally substituted with halo, nitro, or R_4 ;

or an agronomic salt thereof;

provided that when A is $-NH-C(X)R_4$ and B is $-C(R_2)_3$, the compound is not

2-(1,1-diethoxyethyl)-3-(chloroacetamido)4-methylthiophene;

further provided that when A is $-C(X)$ amine and B is $-Q(R_2)_3$ where Q is Si, Ge, or Sn, the compound is not

2-(tert-butylaminocarbonyl)-3-trimethylsilylthiophene,

2-(diethylaminocarbonyl)-3,5-bis(trimethylsilyl)thiophene,
 2-(diethylaminocarbonyl)-3-trimethylsilylthiophene,
 2-(diethylaminocarbonyl)-3-trimethylsilyl-5-(methylthio)thiophene; or
 2-(diethylaminocarbonyl)-3-(methylthio)-5-(trimethylsilyl)thiophene

further provided that when A is -C(X)amine and B is -C(R₃)_pH_(2-p)Q(R₂)₃ where Q is Si, Ge, or Sn, the compound is not

2-(tert-butylaminocarbonyl)-3-(trimethylsilylmethyl)thiophene, or
 2-[N-methyl-N-(tert-butyl)aminocarbonyl]-3-(trimethylsilylmethyl)thiophene;

further provided that when A is -NH-C(X)R₄ and B is -2-naphthyl, the compound is not 2-(2-naphthyl)-3-(methoxycarbonylamino)benzothiophene.

[0014] The term "amine" in -C(X)-amine means an unsubstituted, monosubstituted, or disubstituted amino radical, including nitrogen-bearing heterocycles. Examples of substituents for the amino radical include, but are not limited to, hydroxy; alkyl, alkenyl, and alkynyl, which may be straight or branched chain or cyclic; alkoxyalkyl; haloalkyl; hydroxyalkyl; alkylthio; alkylthioalkyl; alkylcarbonyl; alkoxyalkyl; aminocarbonyl; alkylaminocarbonyl; cyanoalkyl; mono- or dialkylamino; phenyl, phenylalkyl or phenylalkenyl, each optionally substituted with one or more C1-C6 alkyl, alkoxy, haloalkyl, C3-C6 cycloalkyl, halo, or nitro groups; C1-C4 alkyl or alkenyl groups substituted with heterocycles, optionally substituted with one or more C1-C4 alkyl, alkoxy, haloalkyl, halo, or nitro groups. Examples of such nitrogen-bearing heterocycles, which are bonded at a nitrogen to -C(X)-, include, but are not limited to, morpholine, piperazine, piperidine, pyrrole, pyrrolidine, imidazole, and triazoles, each of which may be optionally substituted with one or more C1-C6 alkyl groups.

[0015] Specific examples of the amino radicals useful in the present invention include, but are not limited to, ethylamino, methylamino, propylamino, 2-methylethylamino, 1-propenylamino, 2-propenylamino, 2-methyl-2-propenylamino, 2-propynylamino, butylamino, 1,1-dimethyl-2-propynylamino, diethylamino, dimethylamino, N-(methyl)ethylamino, N-(methyl)-1,1-(dimethyl)ethylamino, dipropylamino, octylamino, N-(ethyl)-1-methylethylamino, 2-hydroxyethylamino, 1-methylpropylamino, chloromethylamino, 2-chloroethylamino, 2-bromoethylamino, 3-chloropropylamino, 2,2,2-trifluoroethylamino, cyanomethyl, methylthiomethylamino, (methylsulfonyl)oxyethylamino, 2-ethoxyethylamino, 2-methoxyethylamino, N-(ethyl)-2-ethoxyethylamino, 1-methoxy-2,2-dimethylpropylamino, cyclopropylamino, cyclobutylamino, cyclopentylamino, cyclohexylamino, methoxymethylamino, N-(methoxymethyl)ethylamino, N-(1-methylethyl)propylamino, 1-methylheptylamino, N-(ethyl)-1-methylheptylamino, 6,6-dimethyl-2-hepten-4-ynylamino, 1,1-dimethyl-2-propynylamino. Further examples include benzylamino, ethylbenzylamino, 3-methoxybenzylamino, 3-(trifluoromethyl)benzylamino, N-methyl-3-(trifluoromethyl)benzylamino, 3,4,5-trimethoxybenzylamino, 1,3-benzodioxol-5-ylmethylamino, phenylamino, 3-(1-methylethyl)phenylamino, ethoxyphenylamino, cyclopentylphenylamino, methoxyphenylamino, nitrophenylamino, 1-phenylethylamino, N-(methyl)-3-phenyl-2-propenylamino, benzotriazolylphenylmethyl, 2-pyridinylmethylamino, N-(ethyl)-2-pyridinylmethylamino, 2-thienylmethylamino, and furylmethylamino. Further examples of amino radicals include methylhydrazino, dimethylhydrazino, N-ethylanilino, and 2-methylanilino. The amine may also be substituted with diethyl N-ethylphosphoramidic acid, t-butoxycarbonyl, methoxycarbonyl, ethoxycarbonyl, propoxycarbonyl, etc. Of these examples of the amino radical, ethylamino is preferred.

[0016] Examples of B include, but are not limited to, trimethylsilyl, ethyldimethylsilyl, diethylmethylsilyl, triethylsilyl, dimethylpropylsilyl, dipropylmethylsilyl, dimethyl-1-(methyl)ethylsilyl, tripropylsilyl, butyldimethylsilyl, pentyldimethylsilyl, hexyldimethylsilyl, cyclopropyldimethylsilyl, cyclobutyldimethylsilyl, cyclopentyldimethylsilyl, cyclohexyldimethylsilyl, dimethylethenylsilyl, dimethylpropenylsilyl, chloromethyldimethylsilyl, 2-chloroethyldimethylsilyl, bromomethyldimethylsilyl, bicycloheptyldimethylsilyl, dimethylphenylsilyl, dimethyl-2-(methyl)phenylsilyl, dimethyl-2-fluorophenylsilyl, and other such silyl groups of the formula Si(R₂)₃; any such silyl group connected to the Z₁-Z₂ ring by a methylene group; and any of these groups wherein germanium or tin is substituted for silicon. Of these examples of B, trimethylsilyl is preferred.

[0017] Further examples of B include 1,1-dimethylethyl, 1,1-dimethylpropyl, 1,1-dimethylbutyl, 1,1-dimethylpentyl, 1-ethyl-1-methylbutyl, 2,2-dimethylpropyl, 2,2-dimethylbutyl, 1-methyl-1-ethylpropyl, 1,1-diethylpropyl, 1,1,2-trimethylpropyl, 1,1,2-trimethylbutyl, 1,1,2,2-tetramethylpropyl, 1,1-dimethyl-2-propenyl, 1,1,2-trimethyl-2-propenyl, 1,1-dimethyl-2-butenyl, 1,1-dimethyl-2-propynyl, 1,1-dimethyl-2-butenyl, 1-cyclopropyl-1-methylethyl, 1-cyclobutyl-1-methylethyl, 1-cyclopentyl-1-methylethyl, 1-(1-cyclopentenyl)-1-methylethyl, 1-cyclohexyl-1-methylethyl, 1-(1-cyclohexenyl)-1-methylethyl, 1-methyl-1-phenylethyl, 1,1-dimethyl-2-chloroethyl, 1,1-dimethyl-3-chloropropyl, 1,1-dimethyl-2-methoxyethyl, 1,1-dimethyl-2-(methylamino)ethyl, 1,1-dimethyl-2-(dimethylamino)ethyl, 1,1-dimethyl-3-chloro-2-propenyl, 1-methyl-1-methoxyethyl, 1-methyl-1-(methylthio)ethyl, 1-methyl-1-(methylamino)ethyl, 1-methyl-1-(dimethylamino)ethyl, 1-chloro-1-methylethyl, 1-bromo-1-methylethyl, and 1-iodo-1-methylethyl. Of these examples of B, 1,1-dimeth-

ylethyl is preferred.

[0018] Further examples of B are 1,1-dimethylethylamino, 1,1-dimethylpropylamino, 1,1-dimethylbutylamino, 1,1-dimethylpentylamino, 1-ethyl-1-methylbutylamino, 2,2-dimethylpropylamino, 2,2-dimethylbutylamino, 1-methyl-1-ethylpropylamino, 1,1-diethylpropylamino, 1,1,2-trimethylpropylamino, 1,1,2-trimethylbutylamino, 1,1,2,2-tetramethylpropylamino, 1,1-dimethyl-2-propenylamino, 1,1,2-trimethyl-2-propenylamino, 1,1-dimethyl-2-butenylamino, 1,1-dimethyl-2-propynylamino, 1,1-dimethyl-2-butyrylamino, 1-cyclopropyl-1-methylethylamino, 1-cyclobutyl-1-methylethylamino, 1-cyclopentyl-1-methylethylamino, 1-(1-cyclopentenyl)-1-methylethylamino, 1-cyclohexyl-1-methylethylamino, 1-(1-cyclohexenyl)-1-methylethylamino, 1-methyl-1-phenylethylamino, 1,1-dimethyl-2-chloroethylamino, 1,1-dimethyl-3-chloropropylamino, 1,1-dimethyl-2-methoxyethylamino, 1,1-dimethyl-2-(methylamino)ethylamino, 1,1-dimethyl-2-(dimethylamino)ethylamino, and 1,1-dimethyl-3-chloro-2-propenylamino. Any of these groups may also have a methyl substitution on the nitrogen, as in N-(methyl)-1,1-dimethylethylamino and N-(methyl)-1,1-dimethylpropylamino. Of these examples of B, 1,1-dimethylethylamino and N-(methyl)-1,1-dimethylethylamino are preferred.

[0019] Further examples of B include 1,1-dimethylethoxy, 1,1-dimethylpropoxy, 1,1-dimethylbutoxy, 1,1-dimethylpentoxy, 1-ethyl-1-methylbutoxy, 2,2-dimethylpropoxy, 2,2-dimethylbutoxy, 1-methyl-1-ethylpropoxy, 1,1-diethylpropoxy, 1,1,2-trimethylpropoxy, 1,1,2-trimethylbutoxy, 1,1,2,2-tetramethylpropoxy, 1,1-dimethyl-2-propenoxy, 1,1,2-trimethyl-2-propenoxy, 1,1-dimethyl-2-butenoxy, 1,1-dimethyl-2-propynyloxy, 1,1-dimethyl-2-butyryloxy, 1-cyclopropyl-1-methylethoxy, 1-cyclobutyl-1-methylethoxy, 1-cyclopentyl-1-methylethoxy, 1-(1-cyclopentenyl)-1-methylethoxy, 1-cyclohexyl-1-methylethoxy, 1-(1-cyclohexenyl)-1-methylethoxy, 1-methyl-1-phenylethoxy, 1,1-dimethyl-2-chloroethoxy, 1,1-dimethyl-3-chloropropoxy, 1,1-dimethyl-2-methoxyethoxy, 1,1-dimethyl-2-(methylamino)ethoxy, 1,1-dimethyl-2-(dimethylamino)ethoxy, 1,1-dimethyl-3-chloro-2-propenoxy. Of these examples of B, 1,1-dimethylethoxy is preferred.

[0020] Further examples of B include 1-methylcyclopropyl, 1-methylcyclobutyl, 1-methylcyclopentyl, 1-methylcyclohexyl, 1-methylcyclopropylamino, 1-methylcyclobutylamino, 1-methylcyclopentylamino, 1-methylcyclohexylamino, N-(methyl)-1-methylcyclopropylamino, N-(methyl)-1-methylcyclobutylamino, N-(methyl)-1-methylcyclopentylamino, and N-(methyl)-1-methylcyclohexylamino.

[0021] R_n may be any substituent(s) which do(es) not unduly reduce the effectiveness of the compounds to function in the method of disease control. R_n is generally a small group; "n" is preferably 2 for thiophene. R is more preferably methyl or halogen, and more preferably is located adjacent to A.

[0022] The present invention also provides novel compounds of the formula given above.

[0023] The invention also provides fungicidal compositions useful in said method.

[0024] As used herein, the term "alkyl", unless otherwise indicated, means an alkyl radical, straight or branched chain, having, unless otherwise indicated, from 1 to 10 carbon atoms. The terms "alkenyl" and "alkynyl" mean unsaturated radicals having from 2 to 7 carbon atoms. Examples of such alkenyl groups include ethenyl, 1-propenyl, 2-propenyl, 1-butenyl, 2-butenyl, 3-butenyl, 2-methyl-1-propenyl, 2-methyl-2-propenyl, 1-methylethenyl, and the like. Examples of such alkynyl groups include ethynyl, 1-propynyl, 2-propynyl, 1,1-dimethyl-2-propynyl, and so forth. Substituent groups may also be both alkenyl and alkynyl, for example, 6,6-dimethyl-2-hepten-4-ynyl.

[0025] As used herein, the term "alkoxy" means an alkyl group having, unless otherwise indicated, from 1 to 10 carbon atoms connected via an ether linkage. Examples of such alkoxy groups include methoxy, ethoxy, propoxy, 1-methylethoxy, and so forth.

[0026] As used herein, the term "alkoxyalkyl" means an ether radical having, unless otherwise indicated, from 1 to 10 carbon atoms. Examples of such alkoxyalkyl groups include methoxymethyl, methoxyethyl, ethoxymethyl, ethoxyethyl, and so forth.

[0027] As used herein, the terms "monoalkylamino" and "dialkylamino" each mean an amino group having, respectively, 1 or 2 hydrogens replaced with an alkyl group.

[0028] As used herein, the term "haloalkyl" means an alkyl radical having one or more hydrogen atoms replaced by halogens, including radicals having all hydrogen atoms substituted by halogen. Examples of such haloalkyl groups are fluoromethyl, difluoromethyl, trifluoromethyl, chloromethyl, trichloromethyl, and so forth.

[0029] As used herein, the term "halo" means a radical selected from chloro, bromo, fluoro, and iodo.

Detailed Description of the Invention

[0030] Control of Gg diseases, including Take-All, using a chemical control agent may be accomplished in several ways. The agent may be applied directly to soil infested with Gg, for example, at the time of planting along with the seed. Alternatively, it may be applied after planting and germination. Preferably, however, it is applied to the seed in a coating prior to planting. This technique is commonly used in many crops to provide fungicides for control of various phytopathological fungi.

[0031] Compositions of the present invention are comprised of a fungicidally effective amount of one or more of the compounds described above and one or more adjuvants. The active ingredient may be present in such compositions

at levels from 0.01 to 95 percent by weight. Other fungicides may also be included to provide a broader spectrum of fungal control. The choice of fungicides will depend on the crop and the diseases known to be a threat to that crop in the location of interest.

[0032] The fungicidal compositions of this invention, including concentrates which require dilution prior to application, may contain at least one active ingredient and an adjuvant in liquid or solid form. The compositions are prepared by admixing the active ingredient with an adjuvant including diluents, extenders, carriers, and conditioning agents to provide compositions in the form of finely-divided particulate solids, granules, pellets, solutions, dispersions or emulsions. Thus, it is believed that the active ingredient could be used with an adjuvant such as a finely-divided solid, a liquid of organic origin, water, a wetting agent, a dispersing agent, an emulsifying agent or any suitable combination of these.

[0033] Suitable wetting agents are believed to include alkyl benzene and alkyl naphthalene sulfonates, sulfated fatty alcohols, amines or acid amides, long chain acid esters of sodium isothionate, esters of sodium sulfosuccinate, sulfated or sulfonated fatty acid esters, petroleum sulfonates, sulfonated vegetable oils, ditertiary acetylenic glycols, polyoxyethylene derivatives of alkylphenols (particularly isooctylphenol and nonylphenol) and polyoxyethylene derivatives of the mono-higher fatty acid esters of hexitol anhydrides (e.g., sorbitan). Preferred dispersants are methyl, cellulose, polyvinyl alcohol, sodium lignin sulfonates, polymeric alkyl naphthalene sulfonates, sodium naphthalene sulfonate, and polymethylene bisnaphthalene sulfonate. Stabilizers may also be used to produce stable emulsions, such as magnesium aluminum silicate and xanthan gum.

[0034] Other formulations include dust concentrates comprising from 0.1 to 60% by weight of the active ingredient on a suitable extender, optionally including other adjuvants to improve handling properties, e.g., graphite. These dusts may be diluted for application at concentrations within the range of from about 0.1-10% by weight.

[0035] Concentrates may also be aqueous emulsions, prepared by stirring a nonaqueous solution of a water-insoluble active ingredient and an emulsification agent with water until uniform and then homogenizing to give stable emulsion of very finely-divided particles. Or they may be aqueous suspensions, prepared by milling a mixture of a water-insoluble active ingredient and wetting agents to give a suspension, characterized by its extremely small particle size, so that when diluted, coverage is very uniform. Suitable concentrations of these formulations contain from about 0.1-60% preferably 5-50% by weight of active ingredient.

[0036] Concentrates may be solutions of active ingredient in suitable solvents together with a surface active agent. Suitable solvents for the active ingredients of this invention for use in seed treatment include propylene glycol, furfuryl alcohol, other alcohols or glycols, and other solvents which do not substantially interfere with seed germination. If the active ingredient is to be applied to the soil, then solvents such as N,N-dimethylformamide, dimethylsulfoxide, N-methylpyrrolidone, hydrocarbons, and water-immiscible ethers, esters, or ketones.

[0037] The concentrate compositions herein generally contain from about 1.0 to 95 parts (preferably 5-60 parts) active ingredient, about 0.25 to 50 parts (preferably 1-25 parts) surface active agent and where required about 4 to 94 parts solvent, all parts being by weight based on the total weight of the concentrate.

[0038] For application to the soil at the time of planting, a granular formulation may be used. Granules are physically stable particulate compositions comprising at least one active ingredient adhered to or distributed through a basic matrix of an inert, finely-divided particulate extender. In order to aid leaching of the active ingredient from the particulate, a surface active agent such as those listed hereinbefore, or for example, propylene glycol, can be present in the composition. Natural clays, pyrophyllites, illite, and vermiculite are examples of operable classes of particulate mineral extenders. The preferred extenders are the porous, absorptive, preformed particles such as preformed and screened particulate attapulgite or heat expanded, particulate vermiculite and the finely-divided clays such as kaolin clays, hydrated attapulgite or bentonitic clays. These extenders are sprayed or blended with the active ingredient to form the fungicidal granules.

[0039] The granular compositions of this invention may contain from about 0.1 to about 30 parts by weight of active ingredient per 100 parts by weight of clay and 0 to about 5 parts by weight of surface active agent per 100 parts by weight of particulate clay.

[0040] The method of the present invention may be carried out by mixing the composition comprising the active ingredient into the seed prior to planting at rates from 0.01 to 50 g per kg of seed, preferably from 0.1 to 5 g per kg, and more preferably from 0.2 to 2 g per kg. If application to the soil is desired, the compounds may be applied at rates from 10 to 1000 g per hectare, preferably from 50 to 500 g per hectare. The higher application rates will be needed for situations of light soils or greater rainfall or both.

[0041] The compounds useful in the present invention may be prepared by methods known to those of ordinary skill in the art. The following examples illustrate some of these methods and are illustrative only; they are not meant to be limiting in any way.

[0042] Unless otherwise indicated, percentages are given as weight/weight. Melting points and boiling points are reported uncorrected. Thin layer chromatography was carried out with varying concentrations of ethyl acetate/hexanes elutions. Tetrahydrofuran and ether solvents were distilled from sodium metal/benzophenone immediately prior to use. N,N,N',N'-(Tetramethyl)-ethylenediamine was distilled from calcium hydride prior to use. All other reagents were pur-

chased from Aldrich or Lancaster and used without purification. A measured physical property is reported for each example or the elemental analysis is given at the end of the examples.

[0043] The following abbreviations have the meanings shown:

5	n-BuLi	n-Butyl lithium
	s-BuLi	sec-Butyl lithium
	t-BuLi	tert-Butyl lithium
	DAST	Diethylaminosulfur trifluoride
	DEAD	Diethyl azodicarboxylate
10	DMF	Dimethylformamide
	DMSO	Dimethylsulfoxide
	TMSCl	Trimethylsilyl chloride
	THF	Tetrahydrofuran
	TMEDA	N,N,N',N'-(tetramethyl)ethylenediamine
15	eq	equivalent(s)
	aq	aqueous
	sat	saturated
	min	minutes
	h	hours
20	MeI	Methyl iodide
	Lawesson's Reagent	[2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane-2,4-disulfide]
	TLC	Thin Layer Chromatography
	HPLC	High Pressure Liquid Chromatography
	RC	Radial Chromatography
25	GLC	Gas-liquid Chromatography
	RT	room temperature
	m.p.	melting point

General Methods

[0044] The phrase "worked up in the usual manner" refers to treatment of the reaction mixture with 10% aq citric acid, extraction with diethyl ether, washing of the combined organic extracts with sat brine solution, drying of the organic extract over MgSO₄, and evaporation to dryness in vacuo to afford the crude product. The phrase "appropriate" means a compound having the substituents desired for the final product of the reaction.

Method A. Ortho-introduction of Electrophiles into N,N-dialkylbenzamides.

[0045] 1.3M s-BuLi in cyclohexane (1.1 to 1.2 molar eq) was added dropwise to a dry-ice/acetone or an ether/liquid nitrogen cooled 1.0M solution of TMEDA (1.0 to 1.2 molar eq) in THF, followed by the dropwise addition of the appropriate N,N-dialkylbenzamide (1.0 eq) in THF. The resulting reaction mixture was stirred for 30-60 min at -78 °C to ensure complete aryl anion formation, then was cooled to <-90°C with an ether/liquid nitrogen bath and quenched by the careful addition of the appropriate electrophile. The reaction was allowed to warm slowly to 0 °C then was worked up in the usual manner. If needed, the crude product was purified by chromatography, recrystallization or distillation.

Method B. Ortho-introduction of Electrophiles into N,N-dialkylbenzamides via Inverse Addition.

[0046] 1.3M s-BuLi in cyclohexane (1.2 eq) was added dropwise to an ether/liquid nitrogen cooled 1.0M solution of TMEDA (1.2 eq) in THF, followed by the dropwise addition of the appropriate N,N-dialkylbenzamide (1.0 eq) in THF. The internal reaction temperature was maintained between -80 and -95 °C during both additions. After addition, the cooling bath was replaced with dry-ice/acetone, and the resulting reaction was stirred at -78 °C for 1 h. This solution was then cannulaed into a solution of an excess of the appropriate electrophile in THF at a rate which maintained the internal reaction temperature below -80 °C with an ether/liquid nitrogen bath. The resulting reaction mixture was slowly allowed to 0 °C then purified in the manner described below for each compound.

Method C. Ortho-introduction of Electrophiles into N-alkylbenzamides.

[0047] 1.3M s-BuLi in cyclohexane (2.1 to 2.2 eq) was added dropwise to a dry-ice/acetone or an ether/liquid nitrogen cooled 1.0M solution of TMEDA (1.0 to 1.2 eq) in THF, followed by the dropwise addition of the appropriate N-alkyl-

benzamide (1.0 eq) in THF. The resulting reaction mixture was stirred for 30-60 min at -78 °C to ensure complete aryl anion formation, then was cooled to ≤-90°C with an ether/liquid nitrogen bath and quenched by the careful addition of the appropriate electrophile. The reaction was allowed to warm slowly to -30 °C then was worked up in the usual manner. If needed, the crude product was purified by chromatography, recrystallization or distillation.

METHOD D. Boronate Coupling Procedure

[0048] The compound of Example f (5.0 g, 27.2 mmol), TMEDA (6.6 g, 57.1 mmol), and THF (100 mL) were stirred at -78 °C under nitrogen, and 1.3M s-BuLi in cyclohexane (44 mL, 57.1 mmol) was added dropwise. The mixture was stirred for 15 min and trimethylborate (3.1 g, 29.9 mmol) was added all at once. The mixture was then stirred at -78 °C for 30 min before warming to RT. It was then poured into 10% HCl (100 mL). This mixture was made basic with sat aq NaHCO₃ and extracted with ether. The aq layer was reacidified and extracted with CH₂Cl₂. The combined organic layers were dried (MgSO₄), concentrated, and recrystallized to yield 4.2 g 4-chloro-2-ethyl-1-hydroxy-1H-2,1-benzazaborol-3(2H)-one as a white solid. m.p. 210-211 °C.

[0049] This compound (1.05 eq) in ethanol (2 mL) is added to an appropriate aryl, benzyl, or vinyl bromide (1 eq) and catalytic tetrakis(triphenylphosphine)-palladium(O) in toluene (20 mL) at RT under nitrogen. Sodium carbonate (4 mL of a 2M aq solution) was then added and the resulting mixture was heated to reflux (4-24 h) and monitored by TLC. The mixture was then cooled to room temperature, diluted with additional toluene (20 mL), filtered through celite/silica, washed with water, dried (MgSO₄), and concentrated. If needed, the crude product was purified by chromatography or recrystallization from ethyl acetate/hexanes.

METHOD E1. Amination of benzoyl chlorides.

[0050] A solution of the appropriate acid chloride (1 eq) in toluene or CH₂Cl₂ was added dropwise to an ice-water cooled solution of the appropriate amine (≥ 2 eq) in the same solvent. The mixture was stirred at RT for 1-16 h until complete by GLC, then was partitioned between ethyl acetate and dilute aq acid. The organic phase was dried (MgSO₄) and concentrated. If needed, the crude product was purified by chromatography, recrystallization or distillation.

METHOD E2. Amination of benzoyl chlorides.

[0051] To a solution of the appropriate amine (>1 eq) in 50 mL CH₂Cl₂ is added an appropriate benzoyl chloride (1 eq) and a catalytic amount of benzyltriethylammonium chloride or pyridine. The mixture is cooled to 5 °C and ≥1 eq NaOH (50% aq) is added. The mixture is stirred from 3-16 h, washed with 10% HCl and water, dried and concentrated. The crude product is purified by chromatography, recrystallization or distillation to afford pure product.

Starting Materials

Example a. 2-Chloro-6-(trimethylsilyl)benzoic acid.

[0052] 2-Chlorobenzoic acid (3.91 g, 25 mmol), THF (60 mL), and TMEDA (8.6 mL, 57 mmol) were stirred under nitrogen and cooled to -100 °C. 1.3M s-BuLi in cyclohexane (0.055 mol, 42.3 mL) was added dropwise keeping the temperature below -80 °C. After the addition was complete, TMSCl (2.7 g, 25 mmol) was added dropwise and the resulting mixture was allowed to stir and slowly warm to -30 °C. 25% citric acid (100 mL) was added and the mixture was extracted with two 50 mL portions of ether, which were then combined and washed three times with water, dried (MgSO₄) and concentrated. The crude product was purified by HPLC, eluting with 2:3 ethyl acetate/hexanes. The product was recovered as a white solid in 63% yield. m.p. 129-131 °C.

Example b. 2-Chloro-6-(trimethylsilyl)benzoyl chloride.

[0053] The compound of Example a (2.4 g, 0.01 mol), thionyl chloride (3.57 g, 0.03 mol), toluene (50 mL), and 1 drop of DMF were stirred at RT overnight. The reaction mixture was twice concentrated under vacuum from toluene (50 mL) to afford the desired product as a brown oil in 100% yield.

Example c. 2-Bromo-6-(trimethylsilyl)benzoic acid.

[0054] 2-Bromobenzoic acid (30.15 g, 150 mmol), THF (400 mL), and diisopropyl amine (33.4 g, 330 mmol) were stirred under nitrogen and cooled to -78 °C. 10M n-BuLi in hexanes (31 mL, 0.31 mol) was then added dropwise, followed by the dropwise addition of TMSCl (17.4 g, 160 mmol). The mixture was allowed to slowly warm to -30 °C,

stirred for 1 h, then was poured into 25% citric acid (100 mL) and stirred for 15 min. The mixture was extracted with two 100 mL portions of ether, which were combined and washed three times with sat aq NaHCO₃ solution. The bicarbonate solution was acidified with 25% citric acid and extracted with three 100 mL portions of ether. These extracts were combined, dried (MgSO₄), and concentrated. The crude product was purified by recrystallization from ether/hexanes, and the desired product was recovered as a white solid in 35% yield. m.p. 139-141 °C.

Example d. 2-Bromo-6-(trimethylsilyl)benzoyl chloride.

[0055] The title compound was prepared from the compound of Example c according to the procedure of Example b.

Example e. N,N-Diethyl-2-chlorobenzamide.

[0056] 2-Chlorobenzoyl chloride is reacted with diethylamine using General Method E1 or E2 to produce the title compound.

Example f. N-Ethyl-2-chlorobenzamide.

[0057] 2-Chlorobenzoyl chloride is reacted with ethyl amine using General Method E1 or E2, to produce the title compound.

Example g. (2-(2,6-difluorophenyl)-4,4-dimethyl-2-oxazoline.

[0058] A solution of 2,6-difluorobenzoyl chloride (50 g, 283 mmol) in CH₂Cl₂ (200 mL) was added rapidly dropwise to an ice water-cooled solution of 2-amino-2-methyl-1-propanol (63.1 g, 708 mmol) in CH₂Cl₂ (400 mL). The resulting mixture was stirred at RT and monitored to completion by GLC, then was extracted twice with 10% HCl and once with sat aq NaHCO₃. The organic phase was dried (MgSO₄), and concentrated to afford 61.9 g N-(1,1-dimethyl-2-hydroxyethyl)-2,6-difluorobenzamide as a white solid.

[0059] This compound (60 g, 283 mmol) was added portionwise to ice water-cooled thionyl chloride (65 mL). The resulting yellow solution was stirred at RT for 1 h, then was poured into stirred ether. The solid was collected and washed with ether, then was partitioned between dilute aq NaOH and ether. This latter ether extract was dried (MgSO₄) and concentrated to afford 52.39 g of the title compound as a white solid, an 88% yield.

Example h. 2-Chloro-6-(trimethylsilyl)phenyl isocyanate.

[0060] The compound of Example b (5.0 mmol) was dissolved in 50 mL acetonitrile and tetrabutylammonium azide (Bu₄N₃) (5.2 mmol) was added. The mixture was stirred at RT for 0.5 h. The solvent was removed and the resulting oil was dissolved in 100 mL toluene. After addition of 100 mL hexane a precipitate was filtered off; the filtrate was concentrated to yield 1.5 g of the title compound.

Example i. 2-Chloro-6-(trimethylsilyl)benzaldehyde.

[0061] A 2.0M solution of borane-dimethylsulfide in THF (100 mL) was added over 15 min to a solution of the compound of Example a (11.4 g, 0.05 mol) THF (200 mL). The mixture was refluxed for two days, quenched with methanol (500 mL), and allowed to stand at RT for 2 days. The solvent was then removed and 2-chloro- α -hydroxy-6-(trimethylsilyl)toluene was recrystallized from hexane as 8.9 g of crystals, an 83% yield. m.p. 40-42 °C.

[0062] This compound (6.4 g, 29.9 mmol) was added to a solution of pyridium chlorochromate (7.5 g) in CH₂Cl₂ (500 mL). The mixture was stirred over 2 days and ether (500 mL) was added. The mixture was filtered through silica gel and the solvent removed under vacuum. Again ether (200 mL) was added and the mixture filtered through silica gel. The solvent was removed to yield the title compound as 6.2 g of an oil, a 98% yield.

Example j. 2-(2,6-difluorophenyl)-2-oxazoline.

[0063] 2,6-Difluorobenzoyl chloride (100 g, 566 mmol) was added dropwise over 2 h to a vigorously stirred and ice water cooled mixture of 2-bromoethyl amine hydrobromide (116.05 g, 566 mmol), benzytriethylammonium chloride (5 g, 22.0 mmol), 10% aq NaOH (680 mL, 1.7 mol), and CH₂Cl₂ (1.5 L). The resulting mixture was stirred at RT overnight, then was washed with water (3 X 200 mL), dried (MgSO₄), concentrated, and kugelrohr distilled to afford 51.8 g of 2-(2,6-difluorophenyl)-2-oxazoline as a colorless oil, a 50% yield.

Example k. N-ethyl t-butylmethyleimine.

[0064] 70% EtNH₂ (20.0 g, 310 mmol) was carefully added to trimethylacetaldehyde (24.35 g, 283 mmol) with ice-water cooling to control the exotherm. When the exotherm ceased, the organic layer was separated and reacted with an additional 70% EtNH₂ (1-2 g). The organic layer was separated and distilled (b.p. 96-98°C) from CaH₂ to afford 28.3 g of N-ethyl t-butylmethyleimine as a colorless oil, an 88% yield.

Examples 1-28

Example 1

N-Ethyl-2-(trimethylsilyl)-3-thiophenecarboxamide.

[0065] A mixture of thiophene-3-carboxylic acid (20.0 g, 178 mmol), thionyl chloride (30 mL, 411 mmol), and catalytic DMF (5 drops) was stirred at RT overnight. This solution was concentrated under vacuum, and stripped several times from toluene to remove all traces of excess thionyl chloride. Ethyl amine hydrochloride (29.03 g, 356 mmol) was then added to a solution of this crude acid chloride dissolved in CH₂Cl₂ (50 mL). Pyridine (31.64 g, 400 mmol) was added, and after 1 h of stirring the reaction was washed with 10% HCl followed with water, dried (MgSO₄), concentrated, and recrystallized from EtOAc/hexanes to give 14.9 g of N-ethyl-3-thiophenecarboxamide as a tan solid, a 76% yield. m.p. 115-117 °C.

[0066] 1.3M s-BuLi in cyclohexane (37.23 mL, 48.4 mmol) was added dropwise to a dry-ice/acetone cooled solution of N-ethyl-3-thiophenecarboxamide (3.41 g, 22 mmol) and TMEDA (5.62 g, 48.4 mmol) in THF (100 mL). After stirring for 30 min at -78°C, TMSCl (5.26 g, 48.4 mmol) was added in a single portion. The reaction was allowed to slowly warm to -10 °C over 1 h, then was quenched with dilute aq citric acid and extracted with ethyl acetate (3X). The combined organic solutions were dried (MgSO₄), concentrated, and purified by HPLC with 3:7 EtOAc/hexanes to give 1.4 g of the title compound as a white solid, a 28% yield. m.p. 114-116 °C.

Example 2

2-Chloro-N-ethyl-4-(trimethylsilyl)-3-thiophene-carboxamide.

[0067] A mixture of 3-thiophenecarboxylic acid (20 g, 178 mmol), thionyl chloride (30 mL), and DMF (5 drops) was stirred overnight, then was concentrated under vacuum and stripped several times from toluene to remove all traces of excess thionyl chloride. Pyridine (31.64 g, 400 mmol) was added dropwise to a mixture of this acid chloride and ethylamine hydrochloride in toluene (5 mL) and CH₂Cl₂ (50 mL). After stirring for 1 h, the reaction was washed with 10% aq HCl followed with water, then was dried (MgSO₄), concentrated, and crystallized from ethyl acetate/hexanes to give 14.9 g of N-ethyl-3-thiophenecarboxamide as a tan solid, a 76% yield. m.p. 115°-117°C.

[0068] A solution of 1.3M s-BuLi in cyclohexane (44 mL, 57.2 mmol) was added dropwise to a -78 °C cooled solution of N-ethyl-3-thiophenecarboxamide (4.04 g, 26 mmol) and TMEDA (6.65 g, 57.2 mmol) in THF (100 mL). After stirring for 30 min at -78 °C, a solution of hexachloroethane (13.54 g, 57.2 mmol) in THF (20 mL) was added dropwise. The resulting reaction mixture was warmed to RT over 1h, quenched with dilute aq citric acid, and extracted with EtOAc (3X). The combined organic extracts were dried (MgSO₄), concentrated, and purified by HPLC with 3:7 EtOAc/hexanes to give 2.8 g of N-ethyl-2-chloro-3-thiophenecarboxamide as a yellow oil, a 57% yield.

[0069] A solution of 1.3M s-BuLi in cyclohexane (16.15 mL, 21 mmol) was added dropwise to an ether/liquid N₂ cooled (-100 °C) solution of N-ethyl-2-chloro-3-thiophenecarboxamide (1.90 g, 10 mmol) and TMEDA (3.17 mL, 21 mmol) in THF (100 mL). After stirring for 30 min at -100 °C, TMSCl (2.28 g, 21 mmol) was added in a single portion. The resulting reaction mixture was warmed to -25 °C over 1 h, quenched with dilute aq citric acid, and extracted with EtOAc (3X). The combined organic extracts were dried (MgSO₄), concentrated, and purified by HPLC with 3:17 EtOAc/hexanes to afford 0.3 g of the title compound as a white solid, an 11% yield. m.p. 46-48 °C.

Examples 3 & 4

Example 3: N-Ethyl-3-(trimethylsilyl)-2-thiophenecarboxamide.

Example 4: N-Ethyl-3,5-bis(trimethylsilyl)-2-thiophenecarboxamide.

[0070]

(a) A mixture of 20 g of 2-thiophenecarboxylic acid and 30 mL thionyl chloride was heated at reflux for 2.5 h, then cooled and concentrated in vacuo to give 21 g of crude 2-thiophenecarboxylic acid chloride as an amber oil.

(b) A solution of 2-thiophenecarboxylic acid chloride (7.3 g, 50 mmol) in 30 mL CH_2Cl_2 was added to 70% ethylamine in water (11 g) at -5°C and the resulting solution was stirred at RT for 18 h. After that, water was added. The organic layer was separated, washed with water, brine, dried and concentrated. Purification of the residue by flash chromatography with 25% ethyl acetate-hexane gave 6.4 g (83.1% yield) of N-ethyl-2-thiophenecarboxamide as a white solid, m.p. $75-78^\circ\text{C}$.

(c) A solution of 2.5M n-BuLi in hexane (18 mL) was added dropwise to a solution of N-ethyl-2-thiophenecarboxamide (3.1 g, 20 mmol) in 50 mL THF at below -65°C under a positive nitrogen atmosphere and the resulting solution was stirred at -70°C for 45 min. After that, TMSCl (9 mL) was added slowly at below -60°C and stirring was continued at below -60°C for 15 min. The solution was allowed to warm to 0°C , then poured into water and extracted with CH_2Cl_2 . The organic layer was separated, washed with brine, dried and concentrated. Flash chromatography of the residue with 5% ethyl acetate-hexane yielded 3.1 g of Example 3 as a white solid, m.p. $81-84^\circ\text{C}$, and 1.1 g of Example 4 as a colorless oil. n_D^{24} 1.5228.

Reference Example (not a compound according to the present invention) N,N-Diethyl-2,4-bis(trimethylsilyl)-3-furancarboxamide.

[0071]

a) To a solution of diisopropylamine (10 g, 0.1 mol) in 90 mL THF under a positive nitrogen atmosphere was added 2.5M n-BuLi in hexane (40 mL, 0.1 mol) at below -20°C and the resulting solution was stirred at below -20°C for 0.5 h, then cooled to -70°C and a solution of 3-furoic acid (5.1 g, 46 mmol) in 50 mL THF was added, maintaining the temperature at below -70°C . After the addition was complete, stirring at -70°C was continued for 1 h. Then 20 mL TMSCl was added dropwise at -70°C and the reaction solution was stirred at -70°C for 0.5 h, then allowed to warm to RT and poured into a mixture of CH_2Cl_2 , ice-water and 2N HCl. The aq layer was separated and extracted with CH_2Cl_2 . The combined organic layers were washed with brine, dried and concentrated to give a mixture of 2-(trimethylsilyl)-3-furoic acid and 2,4-bis(trimethylsilyl)-3-furoic acid.

b) A mixture of 3-furoic acid chlorides (prepared from a mixture of acids (1.4 g) of step a, 6 mL thionyl chloride and a catalytic amount of DMF according to the method of Example 3a) was reacted with 4 g of diethylamine as in Example 3b. The crude mixture was purified by flash chromatography with 10% ethyl acetate-hexane to give 0.1 g of the title compound as a greenish oil. n_D^{25} 1.4812.

Example 5

5-Chloro-N-ethyl-3-(trimethylsilyl)-2-thiophene-carboxamide.

[0072] The title compound was prepared from 5-chloro-2-thiophenecarboxylic acid using the methods of Example 3 yielding 1.5 g as a white solid, m.p. $105-108^\circ\text{C}$.

Example 6

N,N-Diethyl-3-(trimethylsilyl)-2-thiophenecarboxamide.

[0073] To a solution of the compound of Example (1.1 g, 5 mmol) in 10 mL THF under a positive nitrogen atmosphere was added dropwise 2.4 mL 2.5M n-BuLi in hexane at -40°C . Stirring was continued at between -30 and -20°C for 1 h. After that, 2 g ethyl iodide was added dropwise. The resulting reaction solution was allowed to warm to RT, stirred at RT for 18 h and then poured into water and CH_2Cl_2 . The organic layer was separated, washed with brine, dried and concentrated in vacuo. The residue was purified on a silica gel column with 10% ethyl acetate-hexane as eluent to give 1 g of the title compound as a colorless oil. n_D^{25} 1.5218.

Example 7

N-Ethyl-5-methyl-3-(trimethylsilyl)-2-thiophene-carboxamide.

- 5 [0074] The title compound was prepared from 5-methyl-2-thiophenecarboxylic acid using the methods of Example 3 yielding 3.6 g as a white solid. m.p. 112-115 °C.

Example 8

- 10 N-Ethyl-5-iodo-3-(trimethylsilyl)-2-thiophene-carboxamide.

[0075] The compound of Example 3 was reacted with iodine using the method of step c of Example 3 to give 0.5 g of the title compound as a white solid. m.p. 85-88 °C.

- 15 Example 9

N-Ethyl-5-formyl-3-(trimethylsilyl)-2-thiophene-carboxamide.

[0076]

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a) To diisopropylamine (12.6 g, 0.125 mol) in 100 mL THF was added slowly 2.5M n-BuLi in hexane (52 mL, 0.13 mol) at -40 °C and stirred at -40 °C for 0.5 h. The solution was cooled to -60 °C and a solution of the compound of Example 3 (12.1 g) in 60 mL THF was added and stirring was continued at between -50 and -60 °C for 1 h. After that the reaction mixture was poured into ether-dry ice slush and extracted with water. The aq layer was acidified

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with conc HCl and extracted with CH₂Cl₂. The organic layer was washed with brine, dried and concentrated in vacuo to afford 5-[(ethylamino)-carbonyl]-4-(trimethylsilyl)-2-thiophenecarboxylic acid.

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b) To a solution of the acid of step a (3.6 g, 12 mmol) in 30 mL THF was added dropwise 30 mL of 1M of diborane in THF at 0 °C. After the addition was complete, the resulting reaction mixture was stirred at RT for 1 h, then cautiously poured into ice-water and extracted with CH₂Cl₂. The organic water was washed with brine, dried and concentrated in vacuo. The crude product was purified by flash chromatography with 30% ethyl acetate-hexane as eluent to give 2.5 g of N-ethyl-5-(hydroxymethyl)-3-(trimethylsilyl)-2-thiophenecarboxamide.

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c) To the compound of step b (1.3 g, 5 mmol) in 40 mL CH₂Cl₂ containing 1.8 g celite was added 2.4 g pyridinium chlorochromate and the resulting reaction mixture was stirred at RT for 2 h. The CH₂Cl₂ solution was filtered through celite, washed with water, brine, dried and concentrated in vacuo. The residue was purified by flash chromatography with 10% ethyl acetate-hexane to give 1.1 g of the desired product as a light yellow solid, m.p. 62-65 °C.

Example 10

N-Ethyl-5-(methylsulfinyl)-3-(trimethylsilyl)-2-thiophenecarboxamide.

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[0077] To a solution of 3.4 g of a 50:50 mixture of the compound of example 3 and 5-(methylthio)-3-(trimethylsilyl)-2-thiophenecarboxamide (obtained from the reaction of compound of example 3 and methyl methanethiosulfonate using the method of step c of Example 3) in 30 mL methanol was added sodium periodate (1 g, 4 mmol) and the resulting reaction mixture was stirred at RT for 18 h. After that, the solvent was removed in vacuo and the residue was chromatographed on a silica gel column with 10%, 30% and then 70% ethyl acetate-hexane to give 1 g of the title compound as a white solid. m.p. 71-76 °C.

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Example 11

50 N-Ethyl-5-(methylthio)-3-(trimethylsilyl)-2-thiophenecarboxamide.

[0078] To a solution of the compound of Example 10 (0.6 g) and NaI (0.8 g) in 10 mL acetone was added slowly 0.4 mL trifluoroacetic anhydride at 0 °C and the mixture was stirred at 0 °C. for an additional hour. Then CH₂Cl₂ and aq sat sodium meta-bisulfite were added. The organic layer was separated, washed with brine, dried and concentrated. Flash chromatography of the residue with 10% ethyl acetate-hexane gave 0.5 g of the title compound as a white solid. m.p. 58-61 °C.

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Example 12

5-Chloro-N-(2-propenyl)-3-(trimethylsilyl)-2-thiophenecarboxamide.

- 5 **[0079]** The title compound was prepared from 5-chloro-2-thiophenecarboxylic acid and allylamine, followed by reaction with TMSCl using the methods of Example 3 to afford 0.7 g of the title compound as a white solid. m.p. 63-66 °C.

Example 13

10 5-Chloro-N-(2-hydroxyethyl)-3-(trimethylsilyl)-2-thiophenecarboxamide.

[0080] According to the method of step c of Example 3, a solution of 5-chloro-2-thiophenecarboxylic acid (3.3 g, 20 mmol) in THF was reacted with 20 mL 2.5M n-BuLi in hexane and then quenched with 8 mL TMSCl to give crude 5-chloro-3-(trimethylsilyl)-2-thiophenecarboxylic acid.

- 15 **[0081]** This acid and a catalytic amount of DMF in 10 mL thionyl chloride was refluxed for 2 h, then cooled to RT and excess thionyl chloride was removed in vacuo. The crude acid chloride was reacted with 2-aminoethanol according to the method of step b of Example 3 to give 0.9 g of the title compound as a white solid, m.p. 110-114 °C.

Example 14

20 5-Chloro-N-(2-chloroethyl)-3-(trimethylsilyl)-2-thiophenecarboxamide.

- [0082]** A solution of the compound of Example 13 (0.4 g) and 1 mL thionyl chloride in 6 mL CH₂Cl₂ was refluxed for 1 h, then cooled and poured into ice-water. Additional CH₂Cl₂ was added. The organic layer was separated, washed with brine, dried and concentrated. Flash chromatography of the residue with 5% ethyl acetate-hexane as eluent gave 0.4 g of the desired product as a white solid. m.p. 68-72 °C.

Example 15

30 5-Chloro-N-[2[(methylsulfonyl)oxy]ethyl]-3-(trimethylsilyl)-2-thiophenecarboxamide.

- [0083]** To a solution of the compound of Example 13 (0.4 g) and 0.5 mL triethylamine in 10 mL CH₂Cl₂ at 0 °C. was added methanesulfonyl chloride (0.2 mL) and the resulting reaction solution was stirred at RT for 2 h. Water was added and the two layers were separated. The organic solution was washed with brine, dried and concentrated. Purification by flash chromatography with 30% ethyl acetate-hexane gave 0.4 g of product as a white solid. m.p. 82-86 °C.

Example 16

40 5-Bromo-N-ethyl-3-(trimethylsilyl)-2-thiophenecarboxamide.

[0084] The title compound was prepared from the compound of Example 3 and bromine according to step c of Example 3. Purification by flash chromatography with 5% ethyl acetate-hexane gave 0.6 g of the product as a white solid. m.p. 96-98 °C.

Example 17

4-Bromo-N-ethyl-2-(trimethylsilyl)-3-thiophenecarboxamide.

[0085]

- 50 a) To a solution of 3,4-dibromothiophene (15 g, 62 mmol) in 80 mL ether under a positive nitrogen atmosphere was added dropwise 75 mL 1.7M t-BuLi in pentane at below -73 °C and the resulting reaction solution was stirred at -78 °C. for 0.5 h. After that, the ether solution was poured into dry ice and extracted with water. The aq solution was washed with ether and then acidified with concentrated HCl. The solid was filtered and air-dried to give 9 g of 4-bromo-3-thiophenecarboxylic acid, yield 70.3%.
- 55 b) N-Ethyl-4-bromo-3-thiophenecarboxamide was prepared from 4-bromo-3-thiophenecarboxylic acid (7 g, 34 mmol) and 70% ethylamine in water according to steps a and b of Example 3 in 64.5% yield.
- c) A solution of this compound (1.9, 8.1 mmol) in THF was metallated with LDA (prepared by diisopropylamine

and 2.5M of n-BuLi in hexane using the method of the Reference Example) and quenched with TMSCl according to the method of step c of Example 3 to give 1.1 g of the title compound as a white solid in 44.5% yield. m.p. 93-96 °C.

Example 18

5-Bromo-N-ethyl-2-(trimethylsilyl)-3-thiophenecarboxamide.

[0086]

a) To a solution of 3-thiophenecarboxylic acid (7.7 g, 60 mmol) in 70 mL acetic acid was added a solution of 9.6 g bromine in 50 mL acetic acid at RT and stirring was continued at RT for 0.5 h. After that, the reaction mixture was poured into 600 mL ice-water. The precipitate was filtered, washed with water and air-dried to give 7.9 g of 5-bromo-3-thiophenecarboxylic acid.

b) 5-Bromo-N-ethyl-3-thiophenecarboxamide was prepared from 5-bromo-3-thiophenecarboxylic acid (2.1g, 10 mmol) and 70% ethylamine in water according to the methods of steps a and b of Example 3 in 70% yield.

c) The compound of step b (1.3 g, 5.6 mmol) was metallated with LDA (prepared from diisopropylamine and 2.5M n-BuLi in hexane as in the Reference Example) and reacted with TMSCl as in step c of Example 3 to give 70.6% of the title compound as a white solid. m.p. 96-98 °C.

Example 19

N-Ethyl-2,5-bis(trimethylsilyl)-3-thiophenecarboxamide.

[0087] To a solution of 5-bromo-3-thiophenecarboxylic acid in 40 mL THF under a positive nitrogen atmosphere was added dropwise a solution of 9 mL of 2.5M n-BuLi in hexane at below -70 °C and the resulting reaction solution was stirred at -78 °C for 1 h. Then 3.6 mL TMSCl was added at below -70 °C and stirring was continued for 1 h at -78 °C. The solution was allowed to warm to 0 °C and poured into water and washed with ether. The aq layer was separated, acidified with conc HCl and extracted with CH₂Cl₂. The organic solution was dried over MgSO₄ and concentrated to give a mixture of acids.

[0088] The acids were converted to the corresponding ethyl amides as in steps a and b of Example 3 and the mixture was purified by flash chromatography with 10% ethyl acetate-hexane to give 0.4 of the title compound as a white solid. m.p. 106-111 °C.

Example 20

N-Ethyl-2-(trimethylsilyl)-4,5,6,7-tetrahydrobenzo[B]thiophene-3-carboxamide.

[0089]

a) To a mixture of cyclohexanone (20 g, 0.2 mol), ethyl cyanoacetate (22.6 g, 0.2 mol) and sulfur (6.8 g 0.22 mol) in 70 mL absolute ethanol was added rapidly 20 mL diethylamine. The reaction mixture was occasionally cooled with a water bath to maintain the temperature below 60 °C. and then stirred at between 30 to 46 °C. for 2 h. Then water was added. The precipitate was filtered, air-dried and recrystallized from ethanol to give 31 g of ethyl 2-amino-4,5,6,7-tetrahydrobenzo[B]-3-carboxylate.

b) To copper (II) bromide (14 g) and 90% t-butyl nitrite (10 mL) in 40 mL acetonitrile at 50 °C. was added in portions 11 g of the amine of step a, such that the temperature did not exceed 65 °C. After the addition was complete, the resulting reaction mixture was stirred for an additional 0.5 h, then partitioned between water and ethyl acetate. The ethyl acetate solution was then washed with water, brine, dried and concentrated. The crude product was chromatographed with 2% ethyl acetate-hexane to give 6.5 g of a 3:1 mixture of ethyl 2-bromo-4,5,6,7-tetrahydrobenzo[B]thiophene-3-carboxylate and ethyl 4,5,6,7-tetrahydrobenzo[B]thiophene-3-carboxylate.

A solution of the mixture of ethyl esters (5 g) and potassium hydroxide (3 g) in 20 mL ethanol was refluxed for 2 h, cooled and the solvent removed in vacuo. Water was added to the solid and the aq solution was acidified with conc HCl. The solid was filtered, washed with water and air dried to give 3.8g of a mixture of acids.

A mixture of the two acids (3.3 g) and a catalytic amount of DMF in 10 mL thionyl chloride was refluxed for 2 h, then cooled and concentrated in vacuo. This mixture of crude acid chlorides was dissolved in 20 mL CH₂Cl₂ and added to 20 mL 70% ethylamine in water at below -20 °C and the mixture was stirred at RT for 18 h. The organic layer was separated, washed with water, brine, dried and concentrated. Flash chromatography of the crude with 15% ethyl acetate-hexane gave 3.2 g of 2-bromo-N-ethyl-4,5,6,7-tetrahydrobenzo[B]thiophene-3-carboxam-

ide and 0.4 g of N-ethyl-4,5,6,7-tetrahydrobenzo[B]thiophene-3-carboxamide.

c) The 2-bromo compound was reacted with TMSCl according to the method of step c of Example 3. Purification by column chromatography with 12% ethyl acetate-hexane afforded 1.1 g of the title compound as a white solid. m.p. 107-112 °C.

Example 21

4,5-Dimethyl-N-ethyl-2-(trimethylsilyl)-3-thiophenecarboxamide:

[0090] Using the procedures for the synthesis of the compound of Example 20 and methyl ethyl ketone as the starting material, the title compound was obtained as a white solid. m.p. 90-94 °C.

Example 22

N-Ethyl-N-(methylthio)-3-(trimethylsilyl)-2-thiophenecarboxamide.

[0091] To a solution of the compound of Example 3 (1.6 g, 6.5 mmol) in 20 mL THF under a positive nitrogen atmosphere was added dropwise 3 mL of 2.5M n-BuLi in hexane at below -70 °C and the resulting solution was stirred at -78 °C for 1 h. A solution of methyl methanethiosulfonate (0.9 g, 7.1 mmol) in THF was then added dropwise at below -70 °C and stirring was continued for an additional hour at -78 °C. After that, the solution was warmed to 0 °C and poured into water. CH₂Cl₂ was added. The aq layer was separated and extracted with CH₂Cl₂. The combined organic layers were washed with brine, dried (MgSO₄) and concentrated. Purification of the crude on a silica gel column with 10% ethyl acetate-hexane gave 1.2 g of the title compound as a colorless oil. n_D^{24} 1.5519.

Example 23

5-Chloro-N-(methylthio)-N-2-propenyl-3-(trimethylsilyl)-2-thiophenecarboxamide.

[0092] The compound of Example 12 (1.1 g) was reacted with 0.52 g of methyl methanethiosulfonate using procedure described for the preparation of the compound of Example 22. The title compound (0.6 g) was purified by flash chromatography with 2% ethyl acetate-hexane and recovered as a colorless oil. n_D^{25} 1.5698.

Example 24

N-Ethyl-3-(trimethylsilyl)-4,5,6,7-tetrahydrobenzo[B]thiophene-2-carboxamide.

[0093] To 9.4 mL DMF in 30 mL 1,2-dichloroethane was added dropwise 9.3 mL phosphorus oxychloride at below 10 °C. The mixture was allowed to warm to RT and 10.3 mL cyclohexanone in 10 mL 1,2-dichloroethane was added. After the addition, the mixture was heated at 60-65 °C for 3 h, then cooled to RT and a solution of 30 g of sodium acetate in 60 mL water was added at below 20 °C. The organic layer was separated, washed with water, brine and dried.

[0094] To the crude aldehyde in 1,2-dichloroethane was added in 1 portion 9 mL methyl thioacetate, followed by dropwise addition of 20 mL triethylamine. The reaction was exothermic and the mixture was stirred at ambient temperature for 18 h. After that, the organic layer was washed with 3N HCl, water, brine, dried and concentrated.

[0095] To this oil were added 4 mL 20% sodium methoxide in methanol and 60 mL methanol and the resulting solution was heated at reflux for 2 h. The solution was cooled and the solvent was removed in vacuo. Water and CH₂Cl₂ were added. The organic layer was separated, washed with brine, dried and concentrated to give 12.6 g of crude methyl 4,5,6,7-tetrahydrobenzo[B]thiophene-2-carboxylate as an oil.

[0096] A mixture of 2.2 g of this methyl ester and 20 mL of 70% ethylamine in water was stirred at RT for 72 h. After that water and CH₂Cl₂ were added. The organic layer was separated, washed with brine, dried and concentrated to give 2 g of ethyl amide as a light yellow solid, m.p. 133-135 °C.

[0097] The title compound was prepared from this ethyl amide (1.1 g, 5 mmol) and TMSCl according to the method of step c of Example 3. Purification by flash chromatography with 10% ethyl acetate-hexane gave 1 g of the product as a white solid. m.p. 126-128 °C.

Example 25

4,5-Dimethyl-N-ethyl-3-(trimethylsilyl)-2-thiophenecarboxamide.

- 5 [0098] The title compound was prepared from methyl ethyl ketone using the methods of Example 24 and was obtained as a white solid. m.p. 77-80 °C.

Example 26

- 10 5-Chloro-N-hydroxy-N-(1-methylethyl)-3-(trimethylsilyl)-2-thiophenecarboxamide.

- [0099] 5-Chloro-3-(trimethylsilyl)-2-thiophenecarboxylic acid chloride was prepared by the reaction of 1 g 5-chloro-3-(trimethylsilyl)-2-thiophenecarboxylic acid (prepared as in Example 13) and 6 mL thionyl chloride, using the procedure of step a in Example 3. This product was dissolved in CH₂Cl₂ at 0 °C and added to a mixture of N-isopropylhydroxylamine hydrochloride (0.55g, 5 mmol) and 4 g NaHCO₃ in 20 mL CH₂Cl₂ and 20 mL water. The resulting reaction mixture was stirred at RT for additional 3 h. The organic layer was separated, washed with brine, dried and concentrated. The residue was purified by flash chromatography with 8% ethyl acetate/hexane to give 80 mg of the title compound. m.p. 146-150 °C.

20

4	C 52.12, 51.45; H 8.41, 8.32; N 4.68, 4.62.
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BIOLOGICAL ASSAYS

- 25 [0100] The compounds prepared in the above examples have demonstrated control of Gg in one or both of the following test methods. The results are shown in the table below.

In vitro Assay

- 30 [0101] The test compounds (0.25 mL of an appropriate stock solution in acetone) are incorporated into 25 mL minimal media agar [prepared by autoclaving a solution of 17.5 g Czapek Dox broth (Difco), 7.5 g purified agar or Bacto-agar (Difco), and 500 mL distilled/deionized water, and then adding 50 µL of 1 mg/mL thiamine hydrochloride and 50 µL of 1 mg/mL biotin in 5% ethanol] and plates are prepared.

- 35 [0102] Each plate is inoculated by placing in a triangular shape three 4-mm plugs of *Gaeumannomyces graminis* var. *tritici* (Ggt) grown on the minimal media agar described above. The plates are incubated in the dark at 19 - 20 °C for 4 to 5 days. The growth of the fungus is measured as the diameter of the mycelial growth. The result is expressed as Percent Inhibition, calculated as $[1 - ((\text{mm growth on treated plate} - 4)/(\text{mm growth on control plate} - 4))] \times 100$.

In vivo Assay

- 40 [0103] Compounds are tested for control of Ggt on 'Bergen' or 'Anza' varieties of wheat grown in 3-inch square pots containing soil infested with Ggt. The infestation is accomplished by mixing the soil with an inoculum prepared by growing Ggt on 1/4 strength potato dextrose agar (4.875 g potato dextrose agar, 5.0 g Bacto agar, 500 mL distilled, deionized water) in plates and using plugs from the plates to infest sterile oats (400 cc whole oats, 350 mL deionized water, autoclaved). After a one-month incubation period at room temperature, the oats are dried and mixed with the soil at 4% v/v. Four wheat seeds are placed on top of the soil in each pot. The test compounds are prepared as an 1:9 acetone/ water v/v solution containing 0.18% Tween® 20 to provide a treatment rate of 0.5 mg active ingredient per pot, treated with 3 mL test solution per pot. Five pots are used for each treatment level and the controls, which are untreated, inoculated and non-inoculated pots. After one hour drying time, the seeds are covered with more of the appropriate soil and a layer of vermiculite. The pots are placed in a growth chamber and watered each day. After four weeks, each pot is evaluated for evidence of disease by examination of the seminal roots of each plant under a dissecting microscope. A 0 to 5 rating scale having the following meanings is used:

- 55 0 = no runner hyphae or lesions present
 1 = runner hyphae and a few small lesions present on <10% of root system
 2 = runner hyphae and small lesions present on 10 - 25% of root system
 3 = runner hyphae and lesions present on 25 - 50% of root system
 4 = runner hyphae and many, large, coalescing lesions on >50% of root system

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5 = root system and culm completely inundated with lesions and runner hyphae

From each set of five replicates a high and low score is eliminated and a replicate mean is calculated by the average of the remaining three scores. This mean score is then compared to the untreated control score and a percent disease control is calculated. These results are reported in the Table below. If the calculation resulted in "0" or less, as compared to the untreated control, a "N" is shown to indicate no control.

1	44	15	N	
2	100	19	11	
3	100	10	10	
4	100	48	17	60
5	100	97	97	40
6	73	N	N	
7	100	N	N	
8	100	23	3	
9	42	19	19	
10	77	N	N	
11	78	25	14	
12	100	70	13	
13	50	N	7	
14	100	88	2	
15	100	14	5	
16	100	61	21	4
17	61	64	18	
18	100	N	N	
19	100	91	N	4
20	100	100	96	87
21	100	100	95	97
22	100	23	14	0
23	100	48	35	
24	67	10	N	
25	100	93	76	
26	78	71	64	
* Tested at 50 ppm.				

Field Tests

[0104] The compounds of Examples 1-26 are combined with various adjuvants, carriers, and other additives and mixed with wheat and barley seed at rates of from 0.01 to 50 g active ingredient per kg of seed which reduce the incidence of *Gg* in previously infested fields compared to check fields seeded with untreated seed.

[0105] From the foregoing, it will be seen that this invention is one well adapted to attain all the ends and objects hereinabove set forth together with advantages which are obvious and which are inherent to the invention.

[0106] Since many possible embodiments may be made of the invention without departing from the scope thereof, it is to be understood that all matter herein set forth or shown in the accompanying drawings is to be interpreted as illustrative and not in a limiting sense.

Claims

1. A compound of the formula

each R is independently selected from

- d) C1-C4 alkoxy, alkenoxy, alkynoxy, C3-C6 cycloalkyloxy, cycloalkenyloxy, alkylthio, alkylsulfanyl, alkyl-sulfonyl, alkylamino, dialkylamino, alkylcarbonylamino, aminocarbonyl, alkylaminocarbonyl, dialkylamino-carbonyl, alkylcarbonyl, alkylcarbonyloxy, alkoxycarbonyl, (alkylthio)carbonyl, phenylcarbonylamino, phe-nylamino, each optionally substituted with halo;

further provided that when A is -C(X)amine and B is -Q(R₂)₃ where Q is Si, Ge, or Sn, the compound is not

- 2-(tert-butylaminocarbonyl)-3-(trimethylsilylmethyl)thiophene, or

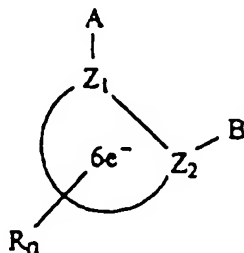
2-[N-methyl-N-(tert-butyl)aminocarbonyl]-3-(trimethylsilylmethyl)thiophene;

further provided that when A is -NH-C(X)R_4 and B is -2-naphthyl, the compound is not 2-(2-naphthyl)-3-(methoxycarbonylamino)benzothiophene.

2. The compound of Claim 1 wherein A is -C(O)-amine , wherein the amino radical is substituted with one or two groups selected from hydroxy; alkyl, alkenyl, and alkynyl, which may be straight or branched chain or cyclic; alkoxy-alkyl; haloalkyl; hydroxyalkyl; alkylthio; alkylthioalkyl; alkylcarbonyl; alkoxyalkyl; aminocarbonyl; alkylaminocarbonyl; cyanoalkyl; mono- or dialkylamino; phenyl, phenylalkyl or phenylalkenyl, each optionally substituted with one or more C1-C4 alkyl, alkoxy, haloalkyl, C3-C6 cycloalkyl, halo, or nitro groups; and C1-C4 alkyl or alkenyl substituted with pyridinyl, thienyl, or furanyl; and wherein the amino radical may be a N-bonded heterocycle selected from morpholine, piperazine, piperidine, pyrrole, pyrrolidine, imidazole, and triazoles, each optionally substituted with C1-C6 alkyl groups.
3. The compound of Claim 1 wherein B is $\text{-Si(R}_2\text{)}_3$.
4. The compound of Claim 1 wherein B is $\text{-O-C(R}_2\text{)}_3$.
5. The compound of Claim 1 wherein B is $\text{-NH-C(R}_2\text{)}_3$ or $\text{-N(CH}_3\text{)-C(R}_2\text{)}_3$.
6. The compound of any of Claims 1-5 wherein each R_2 is independently selected from alkyl, alkenyl, alkynyl, cycloalkyl, haloalkyl, and phenyl, preferably C1-C4 alkyl or haloalkyl, more particularly methyl.
7. The compound of Claim 1 wherein B is 1-naphthyl, 2-naphthyl, or o-tolyl, optionally substituted with halogen or R_4 .
8. The compound of any of Claims 1-7 wherein A is alkylaminocarbonyl or dialkylaminocarbonyl, preferably ethylaminocarbonyl.
9. The compound of any of Claims 1-8 wherein in R_n , n is 1 and R is methyl or halo.
10. The compound of any of Claims 1-9 wherein R is located adjacent to A.
11. The compound 4,5-dimethyl-N-ethyl-2(trimethylsilyl)-3-thiophene carboxamide.
12. A method of controlling disease in a plant caused by *Gaeumannomyces sp.* comprising applying to the plant locus a fungicidally effective amount of a fungicide of any of the claims 1-11.
13. A fungicidal composition for use in the method of Claim 12 comprising an adjuvant and an amount of a compound described therein which is effective to control Take-all.

Patentansprüche

1. Verbindung der Formel



worin

Z_1 und Z_2 für C stehen und Teil eines aromatischen Rings sind, welcher Thiophen ist;
 A ausgewählt wird aus -C(X)-Amin, -C(O)-SR₃, -NH-C(X)R₄ und -C(=NR₃)-XR₇,
 B für -W_m-Q(R₂)₃ steht, oder ausgewählt wird aus o-Tolyl, 1-Naphthyl, 2-Naphthyl und 9-Phenanthryl, jedes
 gegebenenfalls substituiert mit Halogen oder R₄;

Q für C, Si, Ge oder Sn steht;

W für -C(R₃)_pH_(2-p)- steht, wenn Q für Si, Ge oder Sn steht; oder wenn Q für C steht, wird W ausgewählt aus
 -N(R₃)_mH_(1-m)-, -S(O)_p- und -O-;

X für O oder S steht;

n für 0, 1 oder 2 steht;

m für 0 oder 1 steht;

p für 0, 1 oder 2 steht;

jedes R unabhängig ausgewählt wird aus

a) Halogen, Formyl, Cyano, Amino, Nitro, Thiocyanato, Isothiocyanato, Trimethylsilyl und Hydroxy;

b) C1-C4-Alkyl, Alkenyl, Alkynyl, C3-C6-Cycloalkyl und Cycloalkenyl, jedes gegebenenfalls substituiert mit
 Halogen, Hydroxy, Thio, Amino, Nitro, Cyano, Formyl, Phenyl, C1-C4-Alkoxy, Alkylcarbonyl, Alkylthio,
 Alkylamino, Dialkylamino, Alkoxycarbonyl, (Alkylthio)carbonyl, Alkylaminocarbonyl, Dialkylaminocarbo-
 nyl, Alkylsulfinyl oder Alkylsulfonyl;

c) Phenyl, Furyl, Thienyl, Pyrrolyl, jedes gegebenenfalls substituiert mit Halogen, Formyl, Cyano, Amino,
 Nitro, C1-C4-Alkyl, Alkenyl, Alkynyl, Alkoxy, Alkylthio, Alkylamino, Dialkylamino, Halogenalkyl und Halo-
 genalkenyl;

d) C1-C4-Alkoxy, Alkenoxy, Alkinoxy, C3-C6-Cycloalkyloxy, Cycloalkenyloxy, Alkylthio, Alkylsulfinyl, Al-
 kylsulfonyl, Alkylamino, Dialkylamino, Alkylcarbonylamino, Aminocarbonyl, Alkylaminocarbonyl, Dialky-
 laminocarbonyl, Alkylcarbonyl, Alkylcarbonyloxy, Alkoxycarbonyl, (Alkylthio)carbonyl, Phenylcarbonyl-
 amino, Phenylamino, jedes gegebenenfalls substituiert mit Halogen;

worin zwei R-Gruppen vereinigt werden können, um einen kondensierten Ring zu bilden;

jedes R₂ unabhängig ausgewählt wird aus Alkyl, Alkenyl, Alkynyl, Cycloalkyl, Cycloalkenyl und Phenyl, jedes
 gegebenenfalls substituiert mit R₄ oder Halogen; und worin, wenn Q für C steht, R₂ ebenfalls ausgewählt
 werden kann aus Alkoxy, Alkylthio, Alkylamino und Dialkylamino;

worin zwei R₂-Gruppen vereinigt werden können, um eine Cycloalkyl-Gruppe mit Q zu bilden;

R₃ für C1-C4-Alkyl steht;

R₄ für C1-C4-Alkyl, Halogenalkyl, Alkoxy, Alkylthio, Alkylamino oder Dialkylamino steht; und

R₇ für C1-C4-Alkyl, Halogenalkyl oder Phenyl steht, gegebenenfalls substituiert mit Halogen, Nitro oder R₄;
 oder ein agronomisches Salz davon;

vorausgesetzt, dass wenn A für -NH-C(X)R₄ steht und B für -C(R₂)₃ steht, die Verbindung nicht
 2-(1,1-Diethoxyethyl)-3-(chloracetamido)-4-methylthiophen ist;

ferner vorausgesetzt, dass wenn A für -C(X)amin steht und B für -Q(R₂)₃ steht, wo Q für Si, Ge oder Sn steht,
 die Verbindung nicht

2-(tert-Butylaminocarbonyl)-3-trimethylsilylthiophen,

2-(Diethylaminocarbonyl)-3,5-bis(trimethylsilyl)thiophen,

2-(Diethylaminocarbonyl)-3-trimethylsilylthiophen,

2-(Diethylaminocarbonyl)-3-trimethylsilyl-5-(methylthio)thiophen, oder

2-(Diethylaminocarbonyl)-3-(methylthio)-5-(trimethylsilyl)thiophen ist;

ferner vorausgesetzt, dass wenn A für -C(X)amin steht und B für -C(R₃)_pH_(2-p)Q(R₂)₃ steht, wo Q für Si, Ge
 oder Sn steht, die Verbindung nicht

2-(tert-Butylaminocarbonyl)-3-(trimethylsilylmethyl)thiophen oder

2-[N-Methyl-N-(tert-butyl)aminocarbonyl]-3-(trimethylsilylmethyl)thiophen ist;

ferner vorausgesetzt, dass wenn A für -NH-C(X)R₄ steht und B für -2-Naphthyl steht, die Verbindung nicht

2-(2-Naphthyl)-3-(methoxycarbonylamino)benzothiophen ist.

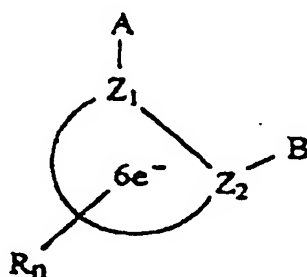
2. Verbindung von Anspruch 1, worin A für -C(O)-Amin steht, worin der Amino-Rest substituiert ist mit einer oder
 zwei Gruppen, ausgewählt aus Hydroxy, Alkyl, Alkenyl und Alkynyl, welche grad- oder verzweigt-kettig oder cyclisch
 sein können; Alkoxyalkyl; Halogenalkyl; Hydroxyalkyl; Alkylthio; Alkylthioalkyl; Alkylcarbonyl; Alkoxycarbonyl; Ami-

nocarbonyl; Alkylaminocarbonyl; Cyanoalkyl; Mono- oder Dialkylamino; Phenyl, Phenylalkyl oder Phenylalkenyl, jedes gegebenenfalls substituiert mit einem oder mehreren C1-C4-Alkyl, Alkoxy, Halogenalkyl, C3-C6-Cycloalkyl, Halogen oder Nitrogruppen; und C1-C4-Alkyl oder Alkenyl substituiert sind mit Pyridinyl, Thienyl oder Furanyl; und worin der Amino-Rest ein N-gebundener Heterocyclus sein kann, ausgewählt aus Morpholin, Piperazin, Piperidin, Pyrrol, Pyrrolidin, Imidazol und Triazolen, jedes gegebenenfalls substituiert mit C1-C6-Alkylgruppen.

3. Verbindung von Anspruch 1, worin B für $-\text{Si}(\text{R}_2)_3$ steht.
4. Verbindung von Anspruch 1, worin B für $-\text{O}-\text{C}(\text{R}_2)_3$ steht.
5. Verbindung von Anspruch 1, worin B für $-\text{NH}-\text{C}(\text{R}_2)_3$ oder $-\text{N}(\text{CH}_3)-\text{C}(\text{R}_2)_3$ steht.
6. Verbindung von einem der Ansprüche 1 bis 5, worin jedes R_2 unabhängig ausgewählt wird aus Alkyl, Alkenyl, Alkynyl, Cycloalkyl, Halogenalkyl und Phenyl, vorzugsweise C1-C4-Alkyl oder Halogenalkyl, insbesondere Methyl.
7. Verbindung von Anspruch 1, worin B für 1-Naphthyl, 2-Naphthyl oder o-Tolyl steht, gegebenenfalls substituiert mit Halogen oder R_4 .
8. Verbindung von einem der Ansprüche 1-7, worin A für Alkylaminocarbonyl oder Dialkylaminocarbonyl, vorzugsweise Ethylaminocarbonyl steht.
9. Verbindung von einem der Ansprüche 1-8, worin in R_n n für 1 steht und R für Methyl oder Halogen steht.
10. Verbindung von einem der Ansprüche 1-9, worin R angrenzend an A lokalisiert ist.
11. Die Verbindung 4, 5-Dimethyl-N-ethyl-2 (trimethylsilyl)-3-thiophencarboxamid.
12. Verfahren zum Bekämpfen einer Krankheit in einer Pflanze, verursacht durch *Gaeumannomyces sp.*, umfassend Aufbringen einer fungizidwirksamen Menge eines Fungizids von einem der Ansprüche 1-11 auf den Pflanzenort.
13. Fungizidzusammensetzung zur Verwendung in dem Verfahren von Anspruch 12, umfassen einen Hilfsstoff und eine Menge von einer hierin beschriebenen Verbindung, welche wirksam zur Bekämpfung von Take-all ist.

Revendications

1. Composé de formule



dans laquelle Z_1 et Z_2 sont C et font partie d'un cycle aromatique qui est le thiophène,
A est choisi parmi $-\text{C}(\text{X})$ -amine, $-\text{C}(\text{O})-\text{SR}_3$, $-\text{NH}-\text{C}(\text{X})\text{R}_4$ et $-\text{C}(=\text{NR}_3)-\text{XR}_7$,
B est $-\text{W}_m-\text{Q}(\text{R}_2)_3$ ou bien est choisi parmi l'o-tolyle, le 1-naphtyle, le 2-naphtyle et le 9-phénantryle, chacun étant facultativement substitué par un halogène ou R_4 ,
Q est C, Si, Ge ou Sn,
W est $-\text{C}(\text{R}_3)_p\text{H}_{(2-p)}$ lorsque Q est Si, Ge ou Sn, ou lorsque Q est C, W est choisi parmi $-\text{N}(\text{R}_3)_m\text{H}_{(1-m)}$, $-\text{S}(\text{O})_p$ et $-\text{O}-$,
X est O ou S,

n prend la valeur 0, 1 ou 2,
 m prend la valeur 0 ou 1,
 p prend la valeur 0, 1 ou 2,
 chaque R est choisi indépendamment à partir de

- a) un groupement halogéno, formyle, cyano, amino, nitro, thiocyanato, isothiocyanato, triméthylsilyle et hydroxy,
 b) un alkyle, un alcényle, un alcynyle (en C1-C4), un cycloalkyle et un cycloalcényle (en C3-C6), chacun substitué facultativement par un groupement halogéno, hydroxy, thio, amino, nitro, cyano, formyle, phényle, un alcoxy, un alkylcarbonyle, un alkylthio, un alkylamino, un dialkylamino, un alcoxycarbonyle, un alkylthiocarbonyle, un alkylaminocarbonyle, un dialkylaminocarbonyle, un alkylsulfinyloxy ou un alkylsulfonyloxy (en C1-C4),
 c) un phényle, un furyle, un thiényloxy, un pyrroloxy, chacun substitué facultativement par un groupement halogéno, formyle, cyano, amino, nitro, un alkyle, un alcényle, un alcynyle, un alcoxy, un alkylthio, un alkylamino, un dialkylamino, un halogénoalkyle et un halogénoalcényle (en C1-C4),
 d) un alcoxy, un alcényle, un alcynyle (en C1-C4), un cycloalkyloxy, un cycloalcényloxy, un alkylthio, un alkylsulfinyloxy, un alkylsulfonyloxy, un alkylamino, un dialkylamino, un alkylcarbonylamino, un aminocarbonyloxy, un alkylaminocarbonyloxy, un dialkylaminocarbonyloxy, un alkylcarbonyloxy, un alcoxycarbonyloxy, un alkylthiocarbonyloxy (en C3-C6), un phénylcarbonylamino, un phénylamino, chacun substitué facultativement par un halogène,

dans lequel deux groupements R peuvent être combinés pour former une combinaison cyclique condensée, chaque R₂ est choisi indépendamment à partir d'un alkyle, d'un alcényle, d'un alcynyle, d'un cycloalkyle, d'un cycloalcényle et d'un phényle, chacun substitué facultativement par R₄ ou un halogène, et dans lequel lorsque Q est C, R₂ peut également être choisi parmi un alcoxy, un alkylthio, un alkylamino et un dialkylamino, dans lequel deux groupements R₂ peuvent être combinés pour former un groupement cycloalkyle avec Q, R₃ est un alkyle (en C1-C4), R₄ est un alkyle, un halogénoalkyle, un alcoxy, un alkylthio, un alkylamino ou un dialkylamino (en C1-C4), et R₇ est un alkyle, un halogénoalkyle (en C1-C4) ou un phényle, substitués facultativement par un halogène, un groupement nitro ou R₄, ou sel agronomique de celui-ci, à la condition que lorsque A est -NH-C(X)R₄ et que B est -C(R₂)₃, le composé n'est pas le 2-(1,1-diéthoxyéthyl)-3-(chloracétamido)-4-méthylthiophène, à la condition en outre que lorsque A est -C(X)-amine et que B est -Q(R₂)₃ où Q est Si, Ge ou Sn, le composé n'est pas

- le 2-(tert-butylaminocarbonyl)-3-triméthylsilylthiophène,
 le 2-(diéthylaminocarbonyl)-3,5-bis(triméthylsilyl)thiophène,
 le 2-(diéthylaminocarbonyl)-3-triméthylsilylthiophène,
 le 2-(diéthylaminocarbonyl)-3-triméthylsilyl-5-méthylthiophène, ou
 le 2-(diéthylaminocarbonyl)-3-(méthylthio)-5-triméthylsilylthiophène,

à la condition en outre que lorsque A est -C(X)-amine et que B est -C(R₃)_pH_(2-p)Q(R₂)₃ où Q est Si, Ge ou Sn, le composé n'est pas

- le 2-(tert-butylaminocarbonyl)-3-triméthylsilylméthylthiophène, ou
 le 2-[N-méthyl-N-(tert-butyl)aminocarbonyl]-3-triméthylsilylméthylthiophène,

à la condition en outre que lorsque A est -NH-C(X)R₄ et que B est -2-naphtyle, le composé n'est pas le 2-(2-naphtyl)-3-méthoxycarbonylaminobenzothiophène.

2. Composé selon la revendication 1, dans lequel A est -C(O)-amine, dans lequel le radical amino est substitué par un ou deux groupements choisis parmi un groupement hydroxy, alkyle, alcényle et alcynyle, qui peuvent être à chaîne droite ou ramifiée ou cycliques, alcoxylalkyle, halogénoalkyle, hydroxylalkyle, alkylthio, alkylthioalkyle, alkylcarbonyl, alcoxycarbonyl, aminocarbonyl, alkylaminocarbonyl, cyanoalkyle, mono- ou dialkylamino, phényle, phénylalkyle ou phénylalcényle, chacun substitué facultativement par un ou plusieurs groupements alkyle, alcoxy, halogénoalkyle (en C1-C4), cycloalkyle (en C3-C6), halogéno ou nitro, et alkyle ou alcényle (en C1-C4) substitués par un pyridinyle, thiényloxy ou furanyloxy, et dans lequel le radical amino peut être un hétérocycle à liaison

N choisi parmi la morpholine, la pipérazine, la pipéridine, le pyrrole, la pyrrolidine, l'imidazole et les triazoles, chacun substitué facultativement par des groupements alkyle (en C1-C6).

3. Composé selon la revendication 1, dans lequel B est $-Si(R_2)_3$.

4. Composé selon la revendication 1, dans lequel B est $-O-C(R_2)_3$.

5. Composé selon la revendication 1, dans lequel B est $-NH-C(R_2)_3$ ou $-N(CH_3)-C(R_2)_3$.

6. Composé selon l'une quelconque des revendications 1 à 5, dans lequel chaque R_2 est choisi indépendamment parmi un alkyle, un alcényle, un alcynyle, un cycloalkyle, un halogénoalkyle et un phényle, de préférence un alkyle ou un halogénoalkyle (en C1-C4), de façon plus particulière le méthyle.

7. Composé selon la revendication 1, dans lequel B est le 1-naphtyle, le 2-naphtyle ou l'o-tolye, substitué facultativement par un halogène ou R_4 .

8. Composé selon l'une quelconque des revendications 1 à 7, dans lequel A est un alkylaminocarbonyle ou un dialkylaminocarbonyle, de préférence l'éthylaminocarbonyle.

9. Composé selon l'une quelconque des revendications 1 à 8, dans lequel dans R_n , n prend la valeur 1 et R est un méthyle ou un halogène.

10. Composé selon l'une quelconque des revendications 1 à 9, dans lequel R est situé de façon contiguë à A.

11. Composé 4,5-diméthyl-N-éthyl-2(triméthylsilyl)-3-thiophène carboxamide.

12. Procédé de traitement de la maladie d'une plante provoquée par *Gaeumannomyces sp.* comprenant l'application à l'emplacement de la plante d'une quantité efficace pour un traitement fongicide d'un fongicide selon l'une quelconque des revendications 1 à 11.

13. Composition fongicide destinée à une utilisation dans le procédé de la revendication 12 comprenant un adjuvant et une certaine quantité d'un composé décrit ici qui est efficace pour traiter le piétin-échaudage.